Conformational analysis by ^{1}H-NMR of chiral cholesteric liquid-crystal polymers: PTOBDME, (R)-PTOBDME and (S)-PTOBDME

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INTRODUCTION

Helical polymers have a current interest due to application in diverses fields as molecular recognition, controlled drug delivery systems, chiral separation mediums or nonlinear optical materials. [1].

Cholesteric liquid crystals polymers present a special mesophase with nematic planes stacked in a helical superstructure with a prevalent screw direction. [2]. The structure chemical of cholesteric polymers is usually fomed by a rigid unit composed by aromatic rings called mesogen, a flexible hydrocarbonated chain and a polar spacer linking the other two parts, in **Fig. 1b.**

Liquid-crystal polymer PTOBDME [C34H36O8]n - poly[terephthaloyl-4-bis-oxybenzoate-decamethyl-ethylene], in **Fig. 1a**, was obtained as cholesteric by polycondensation reaction between terephthaloyl-bis-(4-oxybenzoyl chloride) and DL-1,2-dodecanediol, both racemic materials [3]. The polymer is obtained in two fractions, with different kinetics rates. It presents optical activity, even higher in the second portion.

EXPERIMENTAL

NMR Characterization

A ^{1}H spectra set of PTOBDME in **Fig. 2** obtained starting of racemic 1,2 dodecanediol are compared with enantiomerically pure polymers R-PTOBDME synthesized from R (+)-1,2-dodecanediol and S-PTOBDME synthesized from S (-)-1,2-dodecanediol. The solvent used in all cases was DMSO-d6 from Merck KgaA (Darmstad, Germany). The spectra were performed in a 400 MHz Varian Magnet, processed and analyzed with the help of software MESTREC 4.4.6 [4].

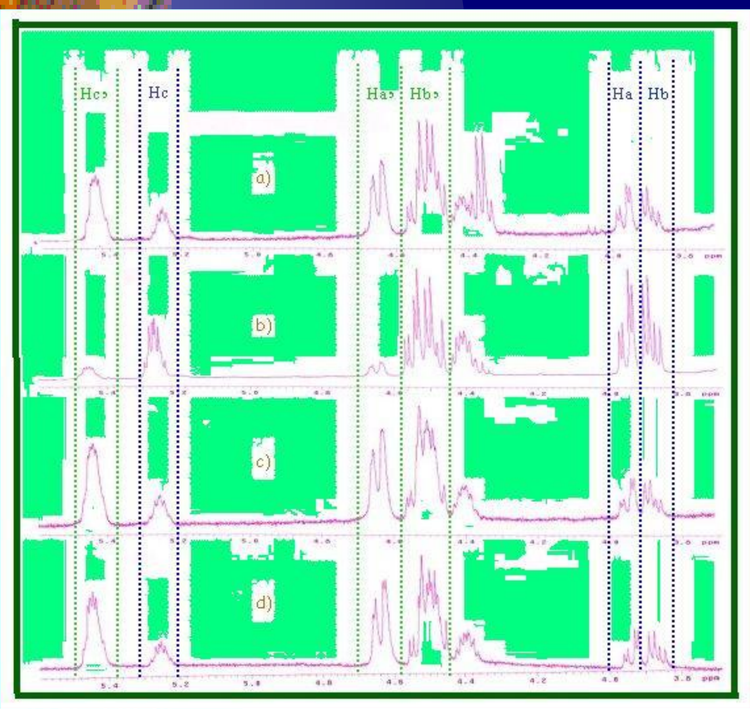


Fig.2 Ampliation of ^{1}H NMR spectra of spacer region of a) PTOBDME of 6 hours of reaction b) PTOBDMEOF 3 hours of reaction, third precipitation c) S-PTOBDME and d) R-PTOBDME. The signals at 4.4 ppm and the complex multiplet at 4.5 ppm which also contains signal of the H_b' corresponds to the endgroup of the polymer.

RESULTS AND DISCUSSION

In the ^{1}H NMR spectra, in **Fig. 2** the double of signal Expected for this structure are observed. R-PTOBDME, S-PTOBDME and PTOBDME of 6 hours of reaction presents the same pattern of spectrum and PTOBDME have the same signals but with different relative integration. The signals are divided in two independent systems how it is showed in the TOCSY 2D experiment in **Fig. 5**. So two independent structures are distinguished by NMR although only one was expected.

To understand better the cause of this phenomenon, it is studied in the bibliography an easier system as the used by Riguera et al [5] for the determination of the absolute steroechemistry of (S) propanediol by derivatization with the (R) and the (S)-enantiomers of a-methoxyphenylacetic acid (MPA) in **Fig. 6**. They show a great agreement with our experimental data.

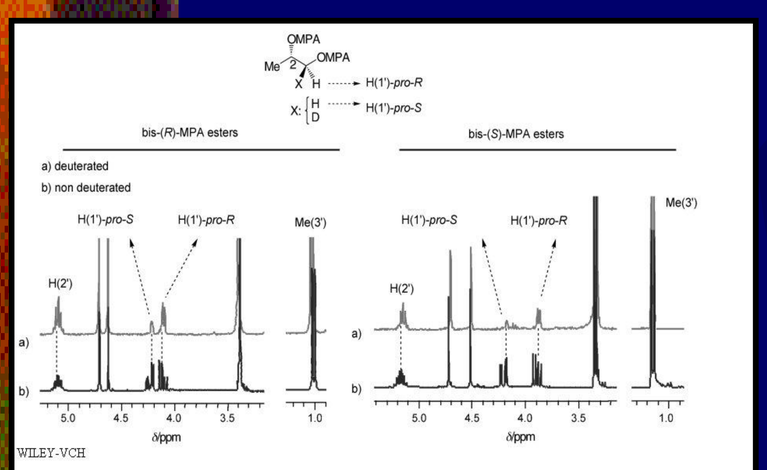


Figure 6. Partial NMR spectra of the bis-MPA-esters of (*S*)-propane-1,2-diol and its (1*S*)-deuterated analogue.

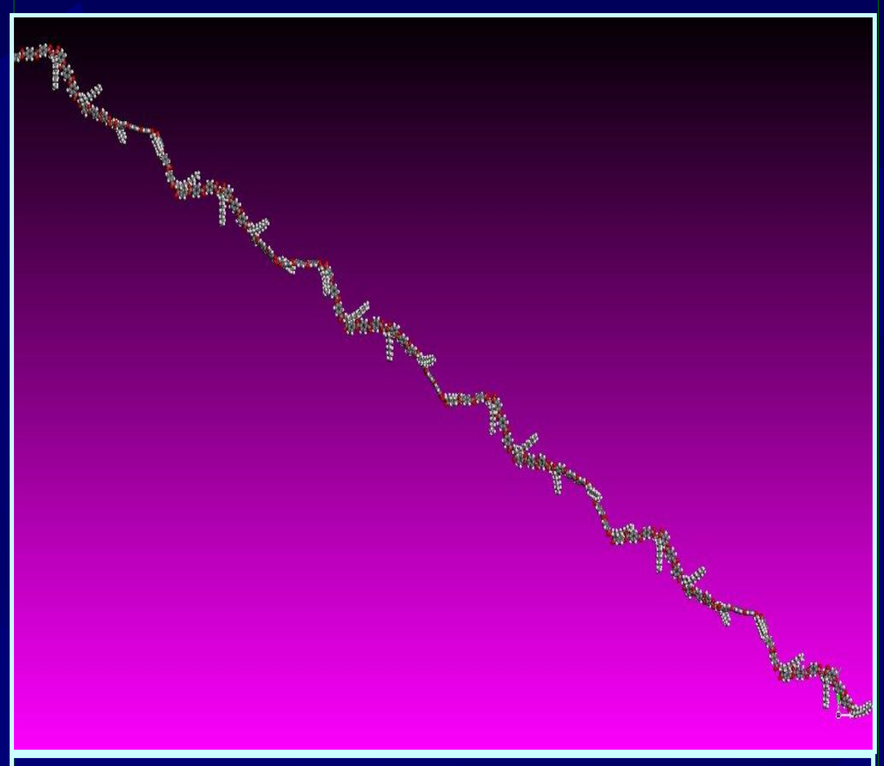


Fig. 1a Isotactic helical PTOBDME generated by 25 monomeric units, with R as absolute configuration of assymetric carbon attached to Hc, and gt as conformation of spacer.

In the case of (S) propanediol derivatized with (R) and (S) MPA the differences between the two spectra of ^{1}H in **Fig. 6**, are caused by the spacial distribution of the substituent groups, in **Fig. 3** c), d). The orientation of phenyl groups are different with respect to the protons H(1)proS, H(1)proR and H(2) in the two diastereromers. They produce different shielding and unshielding effects and the chemical shift of the protons changes with respect one of the other [5].

In the case of PTOBDME, its helical nature (that it was determined by conformational analysis and molecular modeling based on XRD,Raman and transitional thermal analysis [6]), can be the cause of the presence of the double of expected signals. The combination of the different screw-sense (M and P) due to the helical and the configuration R or S of the assymetric carbon attached to Hc generates four diastereomers, or two pair of enantiomers, in **Fig 3** a), b)

The mesogen unit can produce different shielding and unshielding effect in the two pairs of enantiomers and it would make the presence of the double of signals in the ^{1}H NMR spectra.

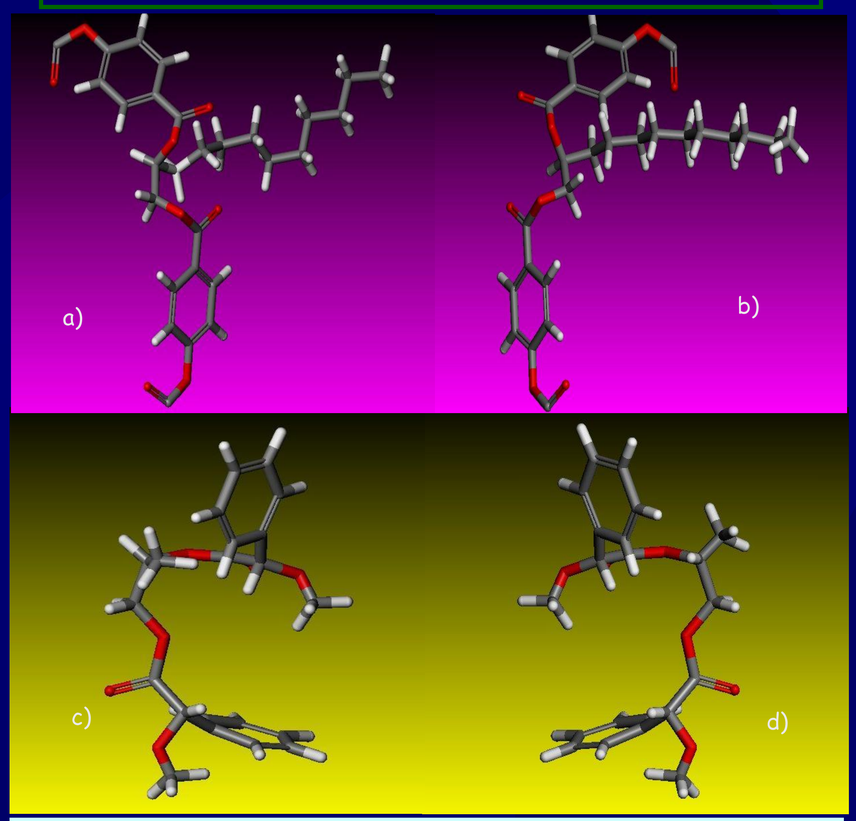


Fig. 3 a) Spacer of R-PTOBDME and b) and the other diasteromer of R-PTOBDME with different screw sense; c) Bis (S) MPA of (R) propanediol and d) Bis (R) MPA of (R) propanediol.
Diasteromers of R-PTOBDME presents an extended helical structure and Bis (R) and Bis (S) MPA of (R) propanediol would present a more close and incomplete helical. The differences and similarity of 1H NMR spectra can be interpretated as function of its spatial distribution.

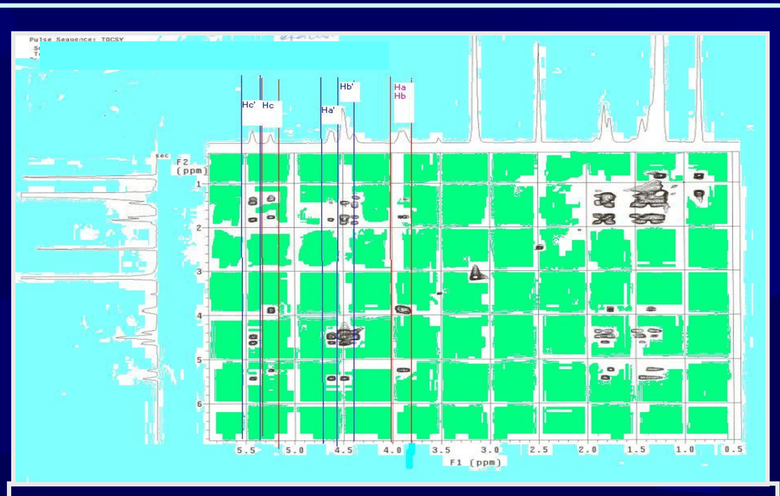
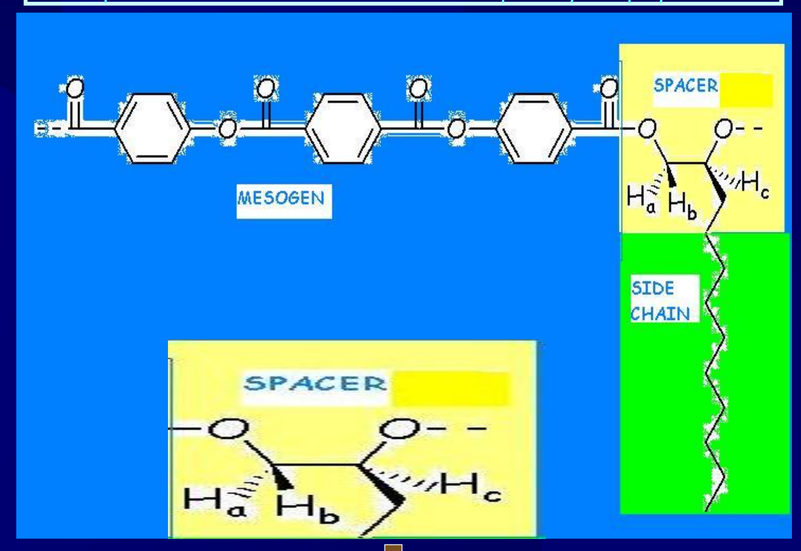


Fig.5 TOCSY 2D of R-PTOBMDE. Red lines indicates the independent system called (not ' system) and blue lines the other system (' system)

Fig.1b. Schematic formula of PTOBDME with the division in mesogen, spacer and side chain of cholesteric liquid crystal polymers



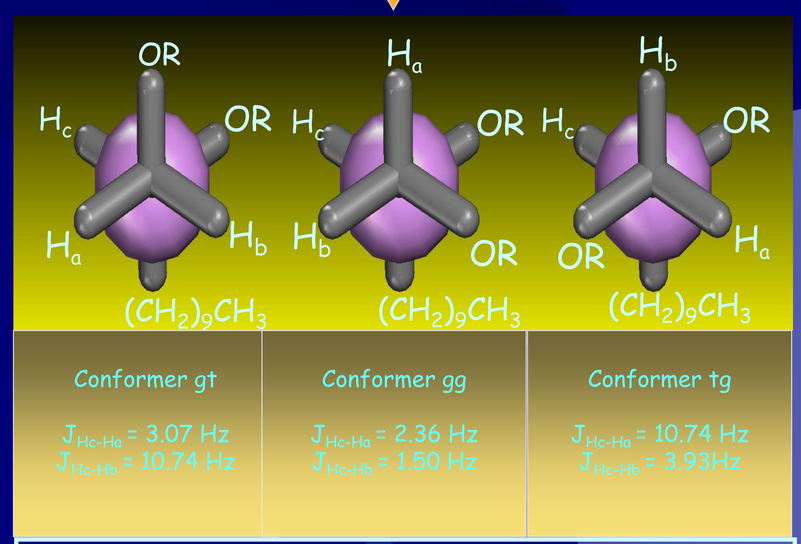


Fig. 4 Newman projection of the different conformers gt, gg and tg of the spacer of R-PTOBDME calculated with [7]

The comformational analysis, in **Fig. 4** perfomed with [7] according to experimental results of vicinal coupling constant J between Hc and Hb and Hc and Ha, indicates us that in the (not ') system, who it has as experimental J_{Hc-Ha} 3.6 Hz and J_{Hc-Hb} 6.3 Hz, the principal conformer is gt. The analysis of (') system is more complex due to the overlapping of Hb', but the experimental $J_{Hc'-Ha'}$ is very low (2 Hz) and it would correspond with a gg conformer.

Besides, the comparison with the diols derivatized with MPA permits us to identifie the protons Ha as HproR and Hb as HproS. They present the same conformer (gt) and the same difference of chemical shift. In the case of Ha' and Hb', they do not present the same principal conformer but the structure of the signals of the spectrum as vicinal coupling as chemical shift are similar and it is very reasonable that they are also HproR and HproS respectively.

CONCLUSIONS.

- ^{1}HNMR spectrum of PTOBMDE presents the double of expected signals.
- The pattern is very similar to the diols derivatized by Bis R and S MPA
- The combination of helical structure and assymetric carbon in the polymer can generate a similar espacial distribution to the presented in the diastereomers formed by diols derivatized by Bis R and S MPA
- By comparison with the diols we can indicate that Ha is HproR and Hb is HproS

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